

1047:796



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Triphenylmethane Dyes

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to certain novel substituted methanes and the dyes obtained therefrom by oxidation. More particularly, it deals with bis(selectively substituted p-aminophenyl)2-thienyl methanes and related methanes in which the 2-thienyl group is replaced by 2-furyl or selectively substituted phenyl. These methanes taken singly are capable of forming, by simple oxidation processes, useful gray to black dyes hitherto unavailable.

A single component gray to black dye is valuable and has significant utility in the graphic arts and textile fields for a number of reasons. In printing applications particularly, a single component black dye is preferred to a black color formed by a mixture of dyes. The single dye can be used without changes of shade resulting from unequal rates of exhaustion of dye components from the ink supply, unequal rates of coloration depending on interaction of components with substrates, and off-shade fading because of differences in the light fastness of the component dyes.

In textile coloration, single component gray to black dyes are also preferred to dye mixtures because they obviate concern with unequal exhaustion from the dye bath, unequal application properties depending on dye component-substrate interaction, unequal fading of components, and off-shade discoloration as a result of laundering or dry cleaning. These latter processes can also affect the components of a dye mixture differently.

In textile dyeing with aromatic amine salts like aniline hydrochloride, a black color can be developed by oxidation. The oxidation of the aromatic amine salts must be carefully taken to the proper stage to avoid off-shades which result from either over- or under-oxidation. Even then, the resultant black dye is a complex mixture of oxidation products which individually are susceptible to varying rates of change by laundering and the action of sunlight and thus cause alterations in the color as do the components of a dye formed by mixing selected colors to give black.

Gray and black shades result from a broad adsorption of visible light and are not commonly attained by single pure dyes. Ideally, to have a neutral shade, a dye should absorb light uniformly in the visible region of the spectrum. In the spectrum of most of the known single organic dyes two or three absorption bands exist, but their positions and intensities are such that the shade imparted to articles dyed or printed with them is a chromatic color. Single dyes which are neutral in shade are generally weak, and much larger quantities of dye are required to produce a black dyeing than are needed to produce blue or red colorations of corresponding depth with the respective blue and red dyes. In order to obtain satisfactory deep gray or black shades, mixtures of dyes must be employed with the complications described above.

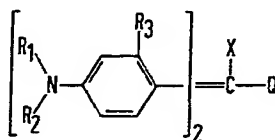
It is clearly desirable to utilize single component gray to black dyes which have

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high tinctorial strength, if these are available. Dyes of high tinctorial strength are found in the realm of basic dyes, and, particularly, in the area of triaryl methane derivatives. True gray and black shades have not, heretofore, been produced by a single dye of this family. In Venkataraman's Synthetic Dyes, Academic Press, Inc., New York, 1952, p. 722, it is stated: "IG claim that blue-black to green-black dyes are obtained when aromatic polyaldehydes, e.g. terephthalaldehyde, or substances which react like aromatic dialdehydes are condensed with secondary or tertiary aromatic amines and the leuco compounds oxidised in the presence of mineral acids. Such deep shades have not so far been obtained with basic dyes of the triphenylmethane class; on the other hand, it has been stated that by condensing terephthaloyl chloride with dimethyl- or diethylaniline, bistriphenylmethane dyes (di-positively charged dyes) are produced which are somewhat yellower in shade than "Malachite Green".

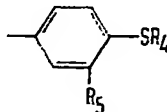
We have now developed certain triphenylmethanes which are colourless but which upon oxidation yield black or gray dyes. Such dyes are of high tinctorial strength and stability.

According to the present invention we provide a leuco dye of the formula I:—



I

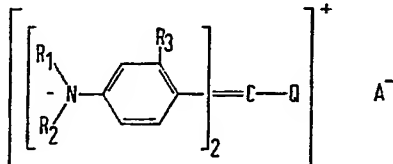
wherein R_1 and R_2 are alkyl groups containing from 1 to 12 carbon atoms, 2-cyanoethyl, 2-hydroxyethyl, 3-hydroxypropyl, alkoxy alkyl groups containing from 2 to 8 carbon atoms, aralkyl or aryl groups, R_3 is methyl, ethyl or fluorine; X is hydrogen, hydroxy or cyano; and Q is 2-thienyl, 2-furyl, 3,4-methylenedioxyphenyl, 2-methoxy-4-(C_1 to C_8)alkoxyphenyl 3,4-di(C_1 to C_8)alkoxyphenyl, or



where R_4 is an alkyl, aralkyl, aryl or substituted aralkyl group containing from 1 to 8 carbon atoms, the substituents of said substituted aralkyl being fluoro, chloro, alkyl or alkoxy substituents and R_5 is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, and coloured oxidised forms thereof.

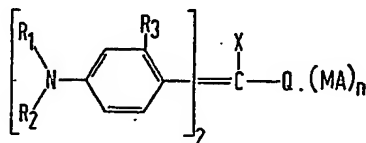
Salts of the above leuco dyes can be made with organic, inorganic or Lewis acids, particularly zinc or ferric chloride. The choice of salt type is dependent on the use to be made of the leuco dyes and their oxidation product (the oxidation product of the leuco dye is the coloured dye). When high water solubility is desired, the hydrochloride leuco dye (which can be oxidised to the chloride salt of the corresponding dye) is preferred. When water insolubility is desired, the phospho-tungstate salts of the dyes are preferred. The latter and other heteropoly acid salts are also more light-fast than the chloride salts of the dyes.

The colored dyes which are formed by oxidation of the leuco dyes or salts thereof have the formula:—



where A is an anion.

The salts of the leuco dyes have the formula: —



where M is hydrogen and A is an organic or inorganic anion, or M is a metal and A is an anion or anions which satisfy the electrovalencies of M and which together with M form a Lewis acid.

The dyes of this invention are single component colouring products which impart gray or black shades to fibres such as cotton, silk, acrylic fibre, to leather, and to paper in any of its many forms. The leuco dyes of this invention and their salts are colourless materials which can be conveniently and selectively converted to coloured materials. Thus, they have application in areas where rapid, simple colour changes are desired, as in photochemical image forming systems as described below.

The new dyes herein described are readily prepared and have high tinctorial strength. They can be used on textiles as gray-to-black self-shades without admixture of other dyes, thus obviating many of the difficulties of mixed shade dyeing. Their high tinctorial value and attractive shades make them useful in graphic arts applications where the brilliance of the conventional triarylmethane dyes, such as Malachite Green, Crystal Violet, and Victoria Blue is disadvantageous because of the unattractive contrast of these colours with papers of nearly every hue. These dyes are thus particularly valuable in printing inks, hectograph compositions, and inks for typewriter ribbons and mimeograph stencils.

Furthermore, these leuco dye compounds are useful in photochemical oxidation processes; for example, the photolysis of hexaarylimidazoles on paper treated with the above leuco dyes leads to gray to black images in the exposed areas. (This photochemical process is described in our co-pending application No. 41215/53) (Serial 1,047,569). With a given amount of leuco dye the density of colour is proportional to the amount of radiation.

The leuco dyes of the present invention are also useful in other photochemical image forming processes including those in which colour is generated when a leuco triarylmethane dye is irradiated in the presence of a halocarbon, such as carbon tetrabromide or hexachloroethane.

The leuco cyanides of this invention became coloured on irradiation with ultra-violet light. In solution, the leuco cyanides are phototropic, i.e., the colour is discharged after standing in the dark. On some substrates, or in the presence of certain anions, such as arylsulphonic acids, these leuco cyanides form permanent colour. Particularly useful compounds for producing a permanent colour are cyanuric acid compounds, including cyanuric acid and cyanuric chloride, but especially cyanuric acid esters as disclosed in U.S. Patent 3,079,258.

When used in the photochemical process described in our copending application, the leuco dye is used in the form where X is H. (hydrogen attached to the central methane carbon atom). The leuco dyes may be used as such or as a salt. The present invention also includes light sensitive compositions which consist of a leuco dye of the above formula where X=H and a 2,4,5 triarylimidazolyl dimer, optionally with an inert solvent and/or an inert, transparent polymeric binder.

The invention also comprehends within its scope a composition which consists of a leuco dye of the above formula and a halocarbon which on exposure to radiation of a suitable wave length generates a halogen-free radical. Carbon tetrabromide is a particularly preferred halocarbon.

Whereas the dyes described in our co-pending application vary in shade from light to dark colours, the dyes of the present invention are useful gray to black dyes hitherto unavailable in their field.

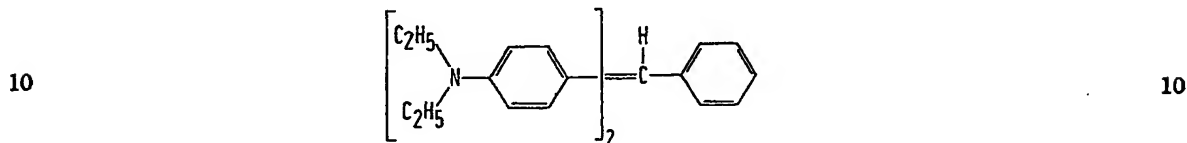
The leuco dyes of the present invention, which upon oxidation are converted to dyes of gray or black shades include the following. These examples are set forth in the form of the free base of the compounds, although the compounds are frequently used in the form of a salt.

1. Bis[4-bis(2-cyanoethyl)amino-o-tolyl](3,4-dibutoxyphenyl)methane.
2. Bis[4-bis(2-cyanoethyl)amino-o-tolyl]2-furylmethane.
3. Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl]2-furylmethane.
4. Bis[4-bis(2-hydroxyethyl)amino-o-tolyl](3,4-dioctyloxyphenyl)cyanomethane.
5. Bis[4-bis(2-hydroxyethyl)amino-o-tolyl]2-furylcyanomethane.
6. Bis[4-bis(3-hydroxypropyl)amino-o-tolyl](2-methoxy-4-octyloxyphenyl)-methane.
7. Bis[4-bis(2-methoxyethyl)amino-o-tolyl](3,4-methylenedioxyphenyl)methane.
8. Bis(4-dibenzylamino-o-tolyl)2-thienylmethane.
9. Bis(4-didodecylamino-o-tolyl)2-furylmethane.
10. Bis(4-diethylamino-2-ethylphenyl)2-furylmethane.
11. Bis(4-diethylamino-2-fluorophenyl)2-furylmethanol.
12. Bis(4-diethylamino-2-fluorophenyl)2-thienylmethane.
13. Bis(4-dimethylamino-2-ethylphenyl)(3,4-methylenedioxyphenyl)methane.
14. Bis(4-dimethylamino-2-ethylphenyl)2-thienylcyanomethane.
15. Bis(4-dimethylamino-2-fluorophenyl)(2,4-dimethoxyphenyl)methanol.
16. Bis(4-dimethylamino-o-tolyl)(2,4-dimethoxyphenyl)methane.
17. Bis(4-dimethylamino-o-tolyl)(3,4-dibutoxyphenyl)methane.
18. Bis(4-dimethylamino-o-tolyl)(3,4-dimethoxyphenyl)methane.
19. Bis(4-dimethylamino-o-tolyl)2-thienylmethane.
20. Bis[4-(N-ethylanilino)-o-tolyl](3,4-methylenedioxyphenyl)cyanomethane.
21. Bis(4-diethylamino-o-tolyl)(3,4-methylenedioxyphenyl)methane.
22. Bis(4-diethylamino-o-tolyl)(2,4-dimethoxyphenyl)methane.
23. Bis(4-diethylamino-o-tolyl)2-furylmethane.
24. Bis(4-diethylamino-o-tolyl)(2-methoxy-4-butoxyphenyl)methanol.
25. Bis(4-diethylamino-o-tolyl)2-thienylmethane.
26. Bis[4-([2-cyanoethyl][2-hydroxyethyl]amino)-o-tolyl]-2-thienylmethane.
27. Bis[4-(N-benzyl-N-ethylamino)-o-tolyl](p-benzylthiophenyl)methane.
28. Bis[4-bis(2-cyanoethyl)amino-o-tolyl](p-benzylthiophenyl)methane.
29. Bis[4-bis(2-ethoxyethyl)amino-o-tolyl](p-benzylthiophenyl)cyanomethane.
30. Bis[4-bis(2-hydroxyethyl)amino-2-ethylphenyl](p-benzylthiophenyl)methane.
31. Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthiophenyl)methane.
32. Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthiophenyl)methane.
33. Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthio-m-butylphenyl)-methane.
34. Bis[4-bis(2-hydroxyethyl)amino-o-tolyl][p-(p-fluorobenzylthiophenyl)-methane.
35. Bis[4-bis(2-hydroxyethyl)amino-o-tolyl](4-benzylthio-m-tolyl)methane.
36. Bis[4-([2-cyanoethyl][2-hydroxyethyl]amino)-o-tolyl](p-benzylthiophenyl)-methane.
37. Bis[4-([2-cyanoethyl][2-hydroxyethyl]amino)-2-ethylphenyl](p-benzylthio-phenyl)methane.
38. Bis(4-dibutylamino-o-tolyl)(p-benzylthiophenyl)methane.
39. Bis(4-didodecylamino-o-tolyl)(p-benzylthiophenyl)methane.
40. Bis(4-diethylamino-2-ethylphenyl)(p-benzylthiophenyl)methane.
41. Bis(4-diethylamino-2-fluorophenyl)(p-benzylthiophenyl)methane.
42. Bis(4-diethylamino-o-tolyl)(p-benzylthiophenyl)cyanomethane.
43. Bis(4-diethylamino-o-tolyl)(p-benzylthiophenyl)methane.
44. Bis(4-diethylamino-o-tolyl)(p-benzylthiophenyl)methanol.
45. Bis(4-diethylamino-o-tolyl)(4-benzylthio-m-tolyl)methane.
46. Bis(4-diethylamino-o-tolyl)[p-(p-chlorobenzylthio)phenyl]methane.
47. Bis(4-diethylamino-o-tolyl)(p-butylthiophenyl)methane.
48. Bis(4-diethylamino-o-tolyl)(p-ethylthiophenyl)methane.
49. Bis(4-diethylamino-o-tolyl)[p-(p-methoxybenzylthio)-phenyl]methanol.
50. Bis(4-diethylamino-o-tolyl)[p-(o-methylbenzylthio)-phenyl]methane.
51. Bis(4-diethylamino-o-tolyl)[p-(p-methylbenzylthio)-phenyl]methane.
52. Bis(4-diethylamino-o-tolyl)(p-methylthiophenyl)methane.
53. Bis(4-diethylamino-o-tolyl)(p-octylthiophenyl)methane.
54. Bis(4-diethylamino-o-tolyl)(p-phenylthiophenyl)methane.
55. Bis(4-diethylamino-o-tolyl)[p-(o-tolylthio)phenyl]methane.
56. Bis(4-dimethylamino-o-tolyl)(p-benzylthiophenyl)methane.
57. Bis(4-dipropylamino-o-tolyl)(p-benzylthiophenyl)methane.
58. Bis[4-(N-[2-ethoxyethyl]-N-ethylamino)-o-tolyl](p-benzylthiophenyl)-methanol.

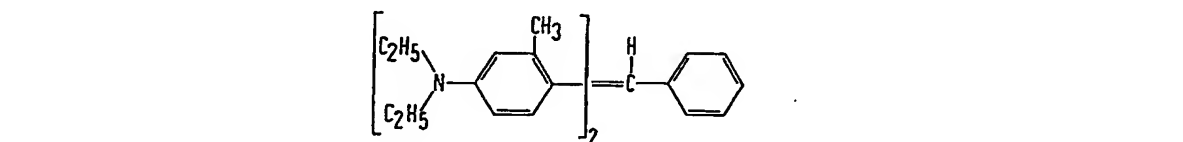
59. Bis[4-(ethylmethylamino)-o-tolyl] (p-benzylthiophenyl)cyanomethane.

60. Bis[4-(N-methylanilino)-o-tolyl] (p-benzylthiophenyl)methanol.

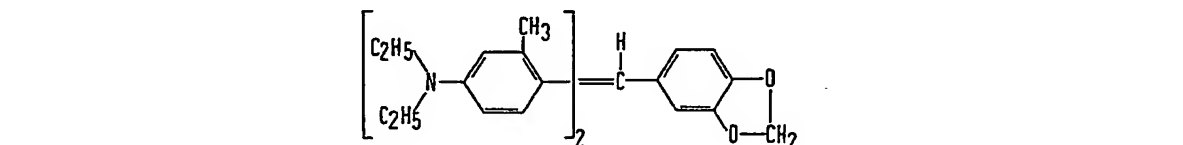
The critical feature of the present novel class of compounds which makes them novel and capable of providing significantly useful colors of gray and black shades is the ethyl, fluoro, or methyl substituent in the 2-position in combination with the disubstituted groups in the 4-position of the two phenyls taken together with one of the designated Q groups. The pronounced and unexpected effect of this combination of substituents is illustrated by the following set of compounds and the colors of their dye products. Bis(4-diethylaminophenyl)phenylmethane,



having neither a substituent in the 2-position of the phenyls bearing the diethylamino groups nor a 3,4-methylenedioxy substituent or 2,4-dialkoxy substituents on the remaining phenyl, yields a green dye. Bis(4-diethylamino-o-tolyl)phenylmethane

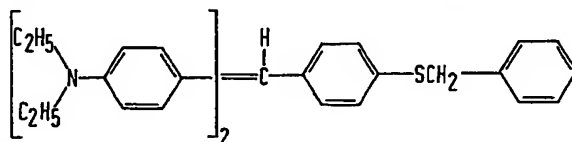


having a methyl substituent in the 2-position of the phenyls bearing the diethylamino groups to give 4-diethylamino-o-tolyl groups, and having no substituent on the remaining phenyl, is oxidized to give a green dye. Bis[4-diethylamino-2-methyl(or ethyl or fluoro)phenyl] (3,4-methylenedioxyphenyl)methane,

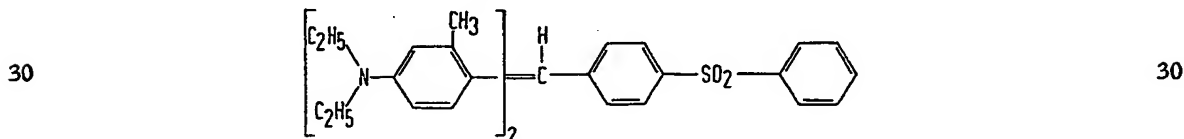


however, having both the proper substituent in the 2-position of the phenyls bearing the p-diethylamino groups and a 3,4-methylenedioxy substituted phenyl, forms a gray dye. Other substituents on the amino nitrogen may be present and the 3,4-methylenedioxyphenyl may be replaced by thienyl, furyl, or a dialkoxyphenyl as shown in formula I and in the list of representative compounds.

25 Bis(4-diethylaminophenyl) (p-benzylthiophenyl)methane,

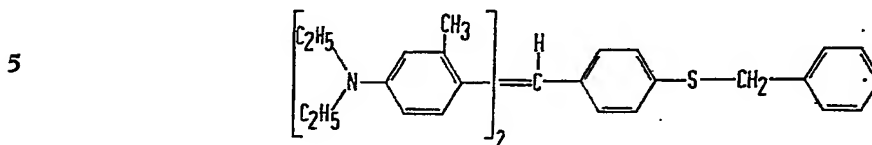


having no substituent in the 2-position of the phenyls bearing the diethylamino groups but having a p-benzylthio substituent in the remaining phenyl, provides also a green dye. Bis(4-diethylamino-o-tolyl) (p-phenylsulfonylphenyl)methane,



having a methyl substituent in the 2-position of the phenyls bearing the diethylamino

groups to give 4-diethylamino-o-tolyls and having no substituted mercapto phenyl attached to the carbon atom, is oxidized to a green dye. A similar compound having the p-phenylsulfonyl replaced by p-diethylamino yields a blue dye. Bis(4-diethylamino-2-methyl (or ethyl or fluoro) phenyl) (p-benzylthiophenyl)methane,



however, having both the selected substituent in the 2-position of the phenyls bearing the p-diethylamino groups and a substituted mercapto group, such as benzylthio, in the p-position of the remaining phenyl, forms a gray dye. Other substituents on the amino nitrogen, other substituents attached to the sulfur of the thiophenyl, and substituents in the 3-position of the phenyl bearing the thio radical may be present as shown in formula I and in the list of representative compounds. But if the methyl, ethyl, or fluoro substituent of bis(4-diethylamino-2-methyl (or ethyl or fluoro) phenyl) (p-benzylthiophenyl)methane is replaced with chlorine, the resulting dye is purple.

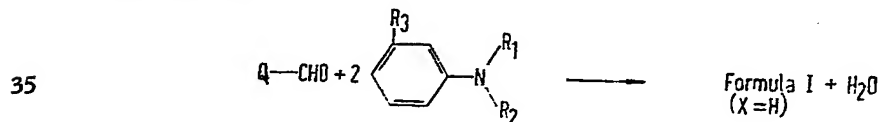
In addition to the selectively substituted methane derivatives, the same derivatives of methanol (X=OH) and cyanomethane (X=CN) are embodied in the invention and provide the same gray and black dyes having high technical value so long as the methanols and cyanomethanes bear such a substituent as methyl, ethyl, or fluorine in the 2-position of the phenyls having di-substituted amino groups in the 4-position and one of the Q groups already defined.

The cationic triphenylmethane type dyes obtained from the invention triphenyl- or (diphenylthienyl or furyl)-methanes, methanols and cyanomethanes are purposely represented by formula III with an apparent trivalent methane carbon atom in recognition of the resonance shifts of electrons that exist in compounds of this type. Several electronic configurations are possible as shown by Krahler in the Chemistry of Synthetic Dyes and Pigments, American Chemical Society Monograph No. 127, page 229, Reinhold Publishing Co., 1955.

Preparation of Compounds and Dyes

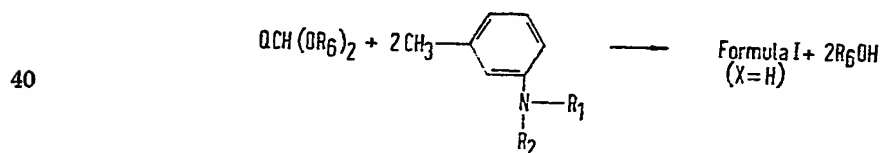
The invention compounds are synthesized by various procedures which have been employed for the preparation of triarylmethane dyes. Of these procedures the following are mentioned as representative of those by which the invention compounds are prepared.

(a) The condensation of 2-thiophenecarboxaldehyde, 2-furaldehyde, or a correspondingly substituted benzaldehyde with an N,N-disubstituted-3-methyl (or ethyl or fluoro)aniline:



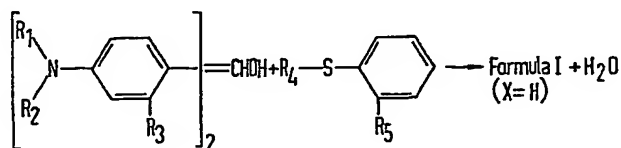
wherein Q and the R's above as well as in the equations below have the same significance as set forth earlier in the specification.

(b) The condensation of an acetal of the aldehydes named in (a) above with an N,N-disubstituted-m-toluidine:



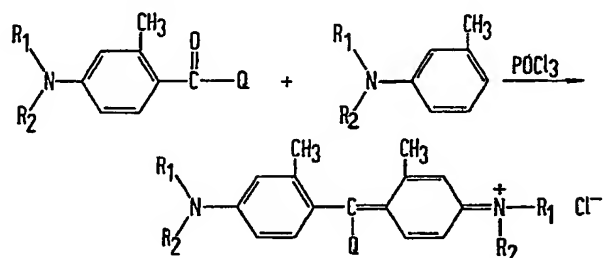
wherein R₆ is methyl or ethyl.

(c) The condensation of a bis[4-N,N-di-substituted amino-2-ethyl (or fluoro or methyl) phenyl]methanol with a phenyl alkyl (or aryl or aralkyl) sulfide:



The corresponding methanols may be prepared by oxidizing the methane derivatives in an alkaline medium, and the corresponding cyanomethanes may be prepared by treating the oxidized dye with an alkali metal cyanide. The methanols may also be prepared directly from the corresponding dye which in turn is prepared from the appropriate ketone and substituted aromatic amine.

Some of the dyes of this invention may also be prepared directly from an appropriately substituted phenone and an N,N-dialkyl-m-toluidine:

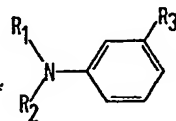


wherein Q and the R's represent the same groups as heretofore defined.

The sequence of reactions for forming the dyes directly as above, is as follows:—

(1) An acid appropriate for forming the Q group of the substituted methane of formula I is converted to the corresponding acid chloride by refluxing in the presence of thionyl chloride. (Organic Syntheses, Collective Vol. 3, John Wiley & Sons, New York, 1955, p. 556).

(2) The acid chloride is then condensed with an aromatic amine of the formula:



shown as part of the formula I in the presence of zinc chloride to form a mixed ketone. (Chemistry of Carbon Compounds, E.H. Rodd, Editor, Vol. III, Part B, Elsevier Publishing Co., 1956, p. 1068).

(3) The mixed ketone is now condensed with the aromatic amine of Step (2) in the presence of phosphorus oxychloride to produce the dye. (The Chemistry of Synthetic Dyes and Pigments, H.A. Lubs, Editor, Reinhold Publishing Corp., New York, 1955, p. 280).

All the dyes of the invention may be produced as illustrated by starting with the carboxylic acid of the Q group of formula I for the sequence of reactions with the indicated substituted aromatic amine.

Once the dye is formed, it may readily be converted independently to its methanol (X=—OH) or cyanomethane (X=CN) derivatives as illustrated in Examples 1 and 7 below.

The present novel substituted methanes, methanols, and cyanomethanes are readily converted to the corresponding dyes by chemical or photochemical processes. Among the chemical processes for converting the substituted methanes to the corresponding dyes are oxidation with lead dioxide (PbO₂), chloranil, sodium dichromate, manganese dioxide, and nitrosyl sulfuric acid in aqueous solution or a solution with an organic solvent. Both the substituted methanols and cyanomethanes are converted to the corresponding dyes by acid hydrolysis. A photochemical process of producing dye consists of exposing to ultra-violet light a mixture of the triphenyl methane compound and a photooxidant preferably in the presence of a small amount of solvent.

Another process consists of irradiating a mixture of the substituted cyanomethanes and a cyanuric acid compound.

The invention dyes may be converted to insoluble salts, referred to as pigment dyes, for the direct colouring or printing of textile fibres and fabrics and for use as pigments for coating compositions by treatment with such an acid as phosphotungstic, phosphomolybdic, phosphotungstomolybdic, and the like. Usually, the dyes exist in a water-soluble cationic form with an anion to balance the positive charge residing in the dye configuration. This anion is obtained from inorganic and organic acids such as, for example, hydrochloric, hydrobromic, hydrofluoric, phosphoric, sulphuric, oxalic, p-toluenesulphonic. The anion may also result from the formation of a zinc chloride complex. This same group of inorganic and organic acids is also used to form salts of the colourless invention triphenylmethane compounds.

In order that the invention may be more fully understood the following Examples are given by way of illustration only:—

EXAMPLE 1

Bis(4-diethylamino-o-tolyl) (3,4-methylenedioxyphenyl)methane

A reactor is charged with 28 parts of isopropyl alcohol, 15 parts of piperonal, and 32.6 parts of N,N-diethyl-m-toluidine. The solution is agitated under nitrogen while 16.2 parts of 98% sulfuric acid is gradually added at a temperature between 30° and 40° C. followed by the addition of 8.4 parts of urea. The reaction mass is heated at 75° C. for four hours and cooled to room temperature. It is then drowned in 400 parts of ice water and the resulting solution is made alkaline to Brilliant Yellow paper with 30% sodium hydroxide solution. The precipitate is collected, washed with water, and slurried in methanol in the presence of activated charcoal. The resultant mixture is filtered. Evaporation of solvent affords 36.8 parts of cream colored powder which is bis(4-diethylamino-o-tolyl) (3,4-methylenedioxyphenyl)-methane.

Dihydrochloride Salt

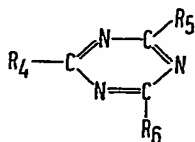
10.0 Parts of the above leuco dye base are slurried in 150 parts of carbon tetrachloride at room temperature, and anhydrous hydrogen chloride is added until no further addition takes place. The off-white solid changes to a gummy precipitate during this period. The solvent is decanted from this precipitate, and then washed with dry ethyl ether. It is then ground in a mortar under ether, to give 11.25 parts of a white powder, which is the dihydrochloride of bis(4-diethylamino-o-tolyl) (3,4-methylenedioxyphenyl)methane.

The above leuco dye dihydrochloride is photochemically oxidised on paper when the latter is immersed briefly in a solution prepared as described below, dried by infrared heat to remove most of the solvent, and irradiated with light of 2537 to 4200 Å. A gray to black colour results on the irradiated portions, the intensity of the colour being a function of the amount of irradiation. The photosensitive composition consisted of:

| | | |
|----|---|----|
| | 1 part leuco dye dihydrochloride | |
| | 1 part dimer of 2-(o-chlorophenyl)-4,5-diphenylimidazolyl | |
| | 20 parts methanol | |
| 45 | 78 parts dimethylformamide. | 45 |

Another method of photolytically generating colour consists of dissolving 1 part of the leuco dye base in 50 parts of carbon tetrabromide, and immersing paper therein for a brief time. Upon drying the paper and irradiating it with light of 2537 Å to 3100 Å a gray to black image results.

A further method of producing colour by irradiating a photosensitive composition with ultraviolet light comprises dissolving one part of the cyanomethane base form of the subject leuco dye and 15 parts of triallylcyanurate in a mixture of 59 parts of dioxane and 25 parts of a 20% solution of cellulose acetate butyrate in a 50—50 mixture of toluene and ethyl acetate. The composition is applied to paper and dried. On exposure to ultraviolet light a gray to black colour is formed. Besides triallylcyanurate may be used a cyanuric acid compound having the formula:



wherein R_1 , R_2 , and R_3 are hydroxy, chlorine, or OY wherein Y is alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl having up to 18 carbon atoms, and preferably where the R groups are the same in any given compound. This group of compounds includes cyanuric acid, cyanuric chloride, trimethylcyanurate, triethylcyanurate, tributylcyanurate, tricyclohexylcyanurate, triphenylcyanurate, tritolylcyanurate, tribenzylcyanurate.

Oxalate Salt

To a solution of 5.4 parts of the subject bis(4-diethylamino-o-tolyl)(3,4-methylenedioxyphenyl)methane in 40 parts of methanol is added a solution of 3.8 parts of oxalic acid dihydrate in 40 parts of methanol. A resinous precipitate forms at once and is isolated for trituration with ethyl ether whereupon a crystalline white solid forms. This is the dioxalate salt of the basic compound.

p-Toluenesulfonate salt

The p-toluene sulfonic acid salt is prepared by a procedure similar to that employed to form the oxalate, but this time using p-toluene sulfonic acid. A crystalline white salt was obtained.

Phosphotungstate Salt

One part of the above dye base is dissolved in a solution of one part of glacial acetic acid in 104 parts of water at 85° C. To this solution is added a hot solution of four parts of sodium tungstate, 0.35 part of disodium phosphate heptahydrate and three parts of 36% hydrochloric acid in 50 parts of water, and the mixed solutions are heated at the boiling point for five minutes. Upon cooling, the insoluble phosphotungstate salt precipitates. It is isolated and washed with water. It dries to a white powder. When dissolved in dimethylformamide to give a 1% solution and applied to paper, the paper is uncolored but upon oxidation with chloranil a gray dye rapidly develops.

Zinc Chloride Salt

Twenty parts of the above leuco dye base are dissolved in 40 parts of water to which 1.2 parts of 36% aqueous hydrochloric acid have been added. To the resultant solution are gradually added 11 parts of zinc chloride dissolved in 20 parts of water. On cooling the mixture the mono zinc chloride derivative of bis(4-diethylamino-o-tolyl)(3,4-methylenedioxyphenyl)methane precipitates and is dried to give 3.5 parts of white product. The product is oxidized with lead dioxide to give a black dye which imparts a gray color to paper.

Oxidation Dye Product

1.6 Parts of the above leuco dye base is dissolved in 25 parts of 1.7% aqueous hydrochloric acid solution at 25° C. and mixed with 0.67 part of lead dioxide. After about three minutes three parts of sodium chloride is added, and the reaction mass is agitated for 30 minutes and filtered. The press cake is dissolved in ten parts of water. 0.17 Part of sodium sulfate is added, the mixture is agitated for 30 minutes, the lead sulfate is separated by filtration, and the dye product is precipitated by the addition of 10% sodium chloride solution. The precipitated dye is collected and dissolved in methanol to separate it from any inorganic material. Evaporation of the solvent yields one part of a black powder which in 0.5% aqueous solution colors paper a gray shade. Absorption spectra in methanolic solution show maxima at 659 mμ and 489 mμ in a ratio of 2.6:1.

This dye and related dyes are useful in hectograph compositions. A mixture of 40 parts of the oxidized leuco dye, bis(4-diethylamino-o-tolyl)(3,4-methylenedioxyphenyl)methane, 40 parts of carnauba wax, and 20 parts of petroleum jelly is rubbed fine, melted at a temperature of about 80° C., and applied as a coating to paper to provide a hectograph master sheet. This master sheet is then used in conventional

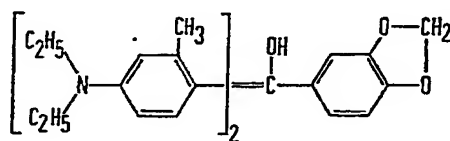
spirit duplicating devices, and dye is transferred to the duplicate sheet by means of volatile alcohol transfer media to give desirable black images.

Phosphotungstate Dye Pigment

5 One part of the above dye is dissolved in 104 parts of water containing one part of glacial acetic acid and treated with sodium tungstate and sodium phosphate under the conditions described above for preparing the phosphotungstate salt of the dye in the reduced state. The dry, black powdery product is the dye pigment. It is insoluble in water, but dissolves in dimethylformamide to provide a solution with which paper is dyed gray. 5

10 Bis(4-diethylamino-o-tolyl) (3,4-methylenedioxyphenyl)methanol

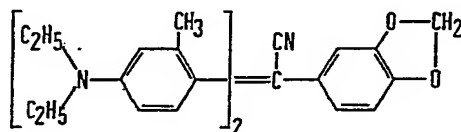
The oxidation dye product of Example 1 in the amount of one part is dissolved in 200 parts of water. The solution is heated to 50° C. and gradually added to 264 parts of 30% aqueous sodium hydroxide solution. When the addition is complete the resultant solution is agitated for about an hour and cooled. The precipitated material, collected and dried at 50° C., amounts to one part of product having the 15 formula 15



20 The presence of the OH group is confirmed by infrared analysis. An acetone solution of the product is essentially colorless. By hydrolysis in acid the original gray dye is obtained. 20

Bis(4-diethylamino-o-tolyl) (3,4-methylenedioxyphenyl)cyanomethane

25 The oxidation dye product of Example 1 in an amount of two parts is dissolved in 100 parts of water, and the solution is blanketed with nitrogen. To the solution is then added 0.4 part of potassium cyanide, and the mixture is agitated for four hours. The precipitate that forms is isolated, washed, and dried and yields 1.4 parts of white powder which has the formula 25



30 Infrared analysis confirms the presence of the $\text{—}\overset{\text{CN}}{\underset{|}{\text{C}}}\text{—}$ group. When a colorless methanol/dimethylformamide solution is applied to paper it produces a colorless spot which on irradiation with ultraviolet light slowly turns gray. 30

EXAMPLE 2

Bis(4-diethylamino-o-tolyl) (3,4-dimethoxyphenyl)methane

35 By the procedure of Example 1, 8.3 parts of 3,4-dimethoxybenzaldehyde and 16.3 parts of N,N-diethyl-m-toluidine are reacted to form the subject compound as a cream colored powder. This product is oxidized with lead peroxide to a black dye, which imparts a gray color to paper treated with an aqueous methanolic solution of it. 35

EXAMPLE 3

Bis(4-diethylamino-o-ethylphenyl) (3,4-methylenedioxyphenyl)methane

40 By the procedure of Example 1, 8 parts of piperonal and 16 parts of N,N-diethyl-m-ethyl-aniline are reacted to form the subject compound as 12 parts of a white powder, which on oxidation affords a gray-to-black dye, which imparts a gray color to paper when dyed with an aqueous solution. 40

EXAMPLE 4

Bis(4-diethylamino-o-fluorophenyl) (3,4-methylenedioxyphenyl)methane

By the procedure of Example 1, 8 parts of piperonal and 16 parts of N,N-diethyl-m-fluoroaniline are reacted to form a white crystalline powder. On oxidation a black powder is formed. An aqueous methanolic solution of the latter imparts a gray color to paper.

EXAMPLE 5

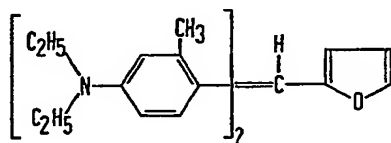
Bis(4-diethylamino-o-tolyl) (2,4-dimethoxyphenyl)methane

By the procedure of Example 1, 8.3 parts of 2,4-dimethoxybenzaldehyde and 16.3 parts of N,N-diethyl-m-toluidine are reacted to form the subject compound as a white crystalline powder. The product is oxidized with lead dioxide to a black dye which imparts a gray color to paper treated with a water or methanol solution of it.

EXAMPLE 6

Bis(4-diethylamino-o-tolyl)2-furylmethane

By the procedure of Example 1, 4.8 parts of 2-furaldehyde and 16.3 parts of N,N-diethyl-m-toluidine are reacted to provide 15 parts of the subject product as a gray powder which, on purification by the usual procedure, gives a product having the formula



with the following analysis:

Calculated for: $C_{27}H_{30}N_2O$: %C=80.2; %H=9.0; %N=6.9.
 Found: %C=80.2; %H=9.1; %N=7.0.

Upon oxidation with lead dioxide this leuco dye base yields a black dye which imparts a gray color to paper. This dye has absorption maxima at $635 m\mu$ and $510 m\mu$ in the ratio of 2.3:1.

EXAMPLE 7

Bis(4-diethylamino-o-tolyl)2-thienylmethane

As in the preceding examples, 5.6 parts of 2-thiophenecarboxaldehyde and 16.3 parts of N,N-diethyl-m-toluidine are reacted to form 18.1 parts of the subject leuco dye having the following analysis.

Calculated for $C_{25}H_{30}N_2S$: %C=77.0; %H=8.5; %N=6.7.
 Found: %C=77.2; %H=8.6; %N=6.2.

On oxidation is formed a black dye which colors paper gray to black.

Oxalate Salt

To a solution of 5.4 parts of the subject bis(4-diethylamino-o-tolyl)-2-thienylmethane in 40 parts of methanol is added a solution of 3.8 parts of oxalic acid dihydrate in 40 parts of methanol. A resinous precipitate forms at once and is isolated for trituration with ethyl ether whereupon a crystalline white solid forms. This is the dioxalate salt of the basic compound.

p-Toluenesulfonate Salt

The p-toluenesulfonic acid salt is prepared by a procedure similar to that employed to form the oxalate, using p-toluenesulfonic acid. A crystalline, white solid is obtained.

Phosphotungstate Salt

One part of the above dye base is dissolved in a solution of one part of glacial acetic acid in 104 parts of water at $85^\circ C$. To this solution is added a hot solution of four parts of sodium tungstate, 0.35 part of disodium phosphate heptahydrate and three parts of 36% hydrochloric acid in 50 parts of water, and the mixed solutions are heated

at the boiling point for five minutes. Upon cooling, the insoluble phosphotungstate salt precipitates. It is isolated and washed with water. It dries to a white powder. When dissolved in dimethylformamide to give a 1% solution and applied to paper, the paper is uncolored but upon oxidation with chloranil a gray dye rapidly develops.

5 Zinc Chloride Salt

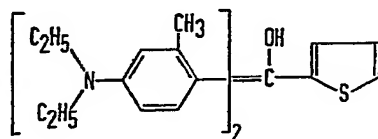
Twenty parts of the above leuco dye base is dissolved in 40 parts of water to which 1.2 parts of 36% aqueous hydrochloric acid have been added. To the resultant solution is gradually added 11 parts of zinc chloride dissolved in 20 parts of water. On cooling the mixture the mono zinc chloride derivative of bis(4-diethylamino-o-tolyl)2-thienylmethane precipitates and is dried to give three parts of white product. The product is oxidized with lead dioxide to give a black dye which imparts a gray color to paper.

Oxidation Dye Product

1.6 Parts of the above leuco dye base is dissolved in 25 parts of 1.7% aqueous hydrochloric acid solution at 25° C. and mixed with 0.67 part of lead dioxide. After about three minutes, three parts of sodium chloride is added and the reaction mass is agitated for 30 minutes and filtered. The press cake is dissolved in ten parts of water. 0.17 Part of sodium sulfate is added, the mixture is agitated for 30 minutes, the lead sulfate is separated by filtration, and the dye product is precipitated by the addition of 10% sodium chloride solution. The precipitated dye is collected and dissolved in methanol to separate it from any inorganic material. Evaporation of the solvent yields one part of a black powder which in 0.5% aqueous solution colors paper a gray shade. The dye has absorption maxima at 659 m μ and 489 m μ in the ratio of 2.6 to 1.

Bis(4-diethylamino-o-tolyl)2-thienylmethanol

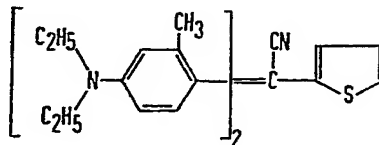
The oxidation dye product in the amount of one part is dissolved in 200 parts of water. The solution is heated to 50° C. and gradually added to 264 parts of 30% aqueous sodium hydroxide solution. When the addition is complete the resultant solution is agitated for about an hour and cooled. The precipitated material, collected and dried at 50° C., amounts to one part of product having the formula



The presence of the OH group is confirmed by infrared analysis. An acetone solution of the product is essentially colorless. By hydrolysis in acid the original gray dye is obtained.

Bis(4-diethylamino-o-tolyl)2-thienylcyanomethane

The oxidation dye product in an amount of two parts is dissolved in 100 parts of water, and the solution is blanketed with nitrogen. To the solution is then added 0.4 part of potassium cyanide, and the mixture is agitated for four hours. The precipitate that forms is isolated, washed, and dried and yields 1.4 parts of white powder which has the formula



Infrared analysis confirms the presence of the $\text{—}\overset{\text{CN}}{\underset{|}{\text{C}}}\text{—}$ group. When a colorless methanol/dimethylformamide solution is applied to paper it produces a colorless spot which on irradiation with ultraviolet light slowly turns gray.

This dye is useful in hectograph compositions. A mixture of 40 parts of the oxidized leuco dye, 40 parts of carnauba wax, and 20 parts of petroleum jelly is rubbed fine, melted at a temperature of about 80° C., and applied as a coating to paper to provide a hectograph master sheet. This master sheet is then used in conventional spirit duplicating devices, and dye is transferred to the duplicate sheet by means of volatile alcohol transfer media to give desirable images.

Phosphotungstate Dye Pigment

One part of the above dye is dissolved in 104 parts of water containing one part of glacial acetic acid and treated with sodium tungstate and sodium phosphate under the conditions described in Example 1.

The dry, black powdery product is the dye pigment. It is insoluble in water, but dissolves in dimethylformamide to provide a solution with which paper is dyed gray.

EXAMPLE 8

Bis[4-([2-cyanoethyl] [2-hydroxyethyl] amino)-o-tolyl]-2-thienylmethane

By the procedure of Example 1, 5.6 parts of 2-thiophenecarboxaldehyde and 19.2 parts of N-(2-cyanoethyl)-N-(2-hydroxyethyl)m-toluidine are reacted to yield 11 parts of the subject compound as a gray powder. On oxidation this leuco dye base produces a black dye which colors paper gray to black.

Additional representative specific compounds which are part of the present generic invention include the following:

bis[4-bis(2-ethoxyethyl)amino-2-fluorophenyl]2-furylcyanomethane

bis[4-bis(4-butoxybutyl)amino-o-tolyl]2-thienylmethane

bis[4-(N-methyl-N-naphthylamino)-o-tolyl] (2,4-dimethoxyphenyl)methane.

EXAMPLE 9

Bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane

A reaction vessel is charged with 40 parts of methanol, 4.9 parts of 35% aqueous hydrochloric acid, 3.0 parts of urea, 16.3 parts of N,N-diethyl-m-toluidine, and 11.4 parts of p-benzylthiobenzaldehyde. The reaction mass is refluxed for 16 hours and then cooled and drowned in 45 parts of water. The resulting solution is made alkaline to Brilliant Yellow paper with sodium hydroxide solution, and 21.5 parts of bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane is precipitated. When washed with cold methanol and dried at 50° C. the white powder melts at 92° to 93° C. and has the following analysis:

Calculated for $C_{30}H_{44}N_2S$: %C=80.5, %H=8.3, %N=5.2, %S=6.0.

Found: %C=80.4, %H=8.1, %N=5.2, %S=5.9.

Dihydrochloride salt

10.0 Parts of the above leuco dye base are slurried in 150 parts of carbon tetrachloride at room temperature, and anhydrous hydrogen chloride is added until no further addition takes place. The white solid changes to a gummy precipitate during this period. The solvent is decanted from this precipitate, and then washed with dry ethyl ether. It is then ground in a mortar under ether, to give 11.25 parts of a white powder, which is the dihydrochloride of bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane.

Calculated for $C_{30}H_{44}N_2S \cdot 2HCl$:

Found:

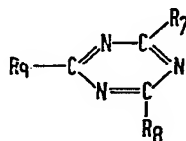
| | | |
|-----|------|------|
| %C | 70.1 | 70.3 |
| %H | 7.6 | 7.5 |
| %N | 4.6 | 4.3 |
| %S | 5.3 | 5.2 |
| %Cl | 11.6 | 11.6 |

The above leuco dye dihydrochloride is photo-chemically oxidised on paper when the latter is immersed briefly in a solution prepared as described below, dried by infrared heat to remove most of the solvent, and irradiated with light of 2537 to 4200 Å. A gray to black colour results on the irradiated portions, the intensity of the colour being a function of the amount of irradiation. The photosensitive composition consists of:

1 part leuco dye dihydrochloride
 1 part dimer of 2-(o-chlorophenyl)-4,5-diphenylimidazolyl
 20 parts of methanol
 78 parts of dimethylformamide.

5 Another method of photolytically generating colour consists of dissolving one part of the leuco dye base in 50 parts of carbon tetrabromide, and immersing paper therein for a brief time. Upon drying the paper and irradiating it with light of 2537 to 3100 Å, a gray to black image results.

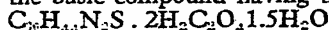
10 A further method of producing colour by irradiating a photosensitive composition with ultraviolet light comprises dissolving one part of the cyanomethane base form of the subject leuco dye and 15 parts of triallylcyanurate in a mixture of 59 parts of dioxane and 25 parts of a 20% solution of cellulose acetate butyrate in a 50—50 mixture of toluene and ethyl acetate. The composition is applied to paper and dried. On exposure to ultraviolet light a gray to black color is formed. Besides triallylcyanurate may be used a cyanuric acid compound having the formula



20 wherein R₇, R₈, and R₉ are hydroxy, chlorine, or OY wherein Y is alkyl, alkenyl, cycloalkyl, aryl, aralkyl or alkaryl having up to 18 carbon atoms, and preferably where the R groups are the same in any given compound. This group of compounds includes cyanuric acid, cyanuric chloride, trimethylcyanurate, triethylcyanurate, tributylcyanurate, tricyclohexylcyanurate, triphenylcyanurate, tritolylcyanurate, tribenzylcyanurate.

Oxalate salt

25 To a solution of 5.4 parts of the subject bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane in 40 parts of methanol is added a solution of 3.8 parts of oxalic acid dihydrate in 40 parts of methanol. A resinous precipitate forms at once and is isolated by trituration with ethyl ether whereupon a crystalline white solid forms. This is the dioxalate salt of the basic compound having the empirical formula



30 confirmed by analysis:

Calculated: %C, 64.6; %H, 6.9; %N, 3.8; %S, 4.3.
 Found: %C, 64.5; %H, 6.6; %N, 3.6; %S, 4.1.

p-Toluenesulfonate Salt

35 The p-toluenesulfonic acid salt is prepared by a procedure similar to that employed to form the oxalate, using p-toluenesulfonic acid. A crystalline, white solid is obtained, having the empirical formula



confirmed by analysis:

40 Calculated: %C, 66.1; %H, 7.0; %N, 3.1; %S, 10.6.
 Found: %C, 66.5; %H, 7.1; %N, 3.1; %S, 10.6.

Zinc Chloride

45 4.0 Parts of the above dye base, i.e., the triphenylmethane derivative, is dissolved in 80 parts of water to which 2.8 parts of 31% aqueous hydrochloric acid solution is added and to the resultant solution is added gradually 22 parts of zinc chloride dissolved in 60 parts of water. On cooling the mixture, the mono zinc chloride derivative of bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane precipitates and is dried to give 6.5 parts of white product, which is oxidized with lead dioxide to give a black dye.

Phosphotungstate salt

One part of the above dye base is dissolved in a solution of one part of glacial acetic acid in 104 parts of water at 85° C. To this solution is added a hot solution of four parts of sodium tungstate, 0.35 part of disodium phosphate heptahydrate and three parts of 36% hydrochloric acid in 50 parts of water, and the mixed solutions are heated at the boiling point for five minutes. Upon cooling, the insoluble phosphotungstate salt precipitates. It is isolated and washed with water. It dries to a white powder. When dissolved in dimethylformamide to give a 1% solution and applied to paper, the paper is uncolored but upon oxidation with chloranil, a gray dye rapidly develops.

Oxidation dye product

The above bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane in an amount of one part is added to 40 parts of methanol with concentrated (36%) hydrochloric acid to effect solution. To this solution is added one part of lead dioxide (PbO₂). The mixture is allowed to react for about five minutes at room temperature, it is filtered, and the filter cake is washed with methanol. Evaporation of the filtrate and washings yields a black powder which is readily soluble in water and methanol. The visible absorption spectrum of solutions of the dye shows strong overlapping absorption bands having maximum absorption at 648 and 499 mμ with an intensity ratio of 2.3. A 0.5% solution of the dye colors paper an attractive gray shade.

This dye and related dyes are useful in hectograph compositions. A mixture of 40 parts of the oxidized leuco dye, bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methane, 40 parts of carnauba wax, and 20 parts of petroleum jelly is rubbed fine, melted at a temperature of about 80° C., and applied as a coating to paper to provide a hectograph master sheet. This master sheet is then used in conventional spirit duplicating devices, and dye is transferred to the duplicate sheet by means of volatile alcohol transfer media to give desirable black images.

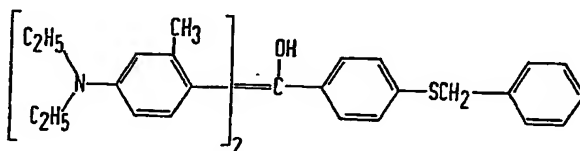
Phosphotungstate dye pigment

One part of the above dye is dissolved in 104 parts of water containing one part of glacial acetic acid and treated with sodium tungstate and sodium phosphate under the conditions described above for preparing phosphotungstate salt of the dye in the reduced state. The dry, black powdery product is the dye pigment. It is insoluble in water, but dissolves in dimethylformamide to provide a solution with which paper is dyed gray.

EXAMPLE 10

Bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)methanol

The oxidation dye product of Example 9 in the amount of one part is dissolved in 200 parts of water. The solution is heated to 50° C. and gradually added to 264 parts of 30% aqueous sodium hydroxide solution. When the addition is complete, the resultant solution is agitated for about an hour and cooled. The precipitated material, collected and dried at 50° C., amounts to one part of product having the formula

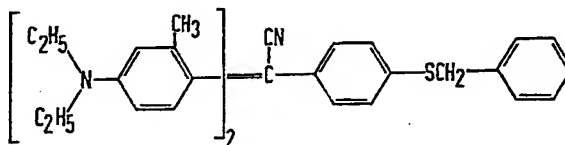


The presence of the OH group is confirmed by infrared analysis. An acetone solution of the product is essentially colorless. By oxidation in acid the original gray dye is obtained.

EXAMPLE 11

Bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl)cyanomethane

The oxidation dye product of Example 9 in an amount of two parts is dissolved in 100 parts of water, and the solution is blanketed with nitrogen. To the solution is then added 0.4 part of potassium cyanide, and the mixture is agitated for four hours. The precipitate that forms is isolated, washed, and dried and yields 1.4 parts of white powder which has the formula

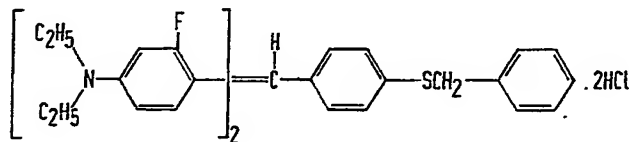


Infrared analysis confirms the presence of the $\text{—}\overset{\text{CN}}{\underset{|}{\text{C}}}\text{—}$ group. When a colorless methanol/dimethylformamide solution is applied to paper it produces a colorless spot which on irradiation with ultraviolet light slowly turns gray.

EXAMPLE 12

Bis(4-diethylamino-2-fluorophenyl) (p-benzylthiophenyl)methane dihydrochloride

A reaction vessel is charged with 80 parts of methanol, 11.4 parts of p-benzylthiobenzaldehyde, and 16.7 parts of N,N-diethyl-m-fluoroaniline. The solution is agitated under nitrogen while 4.9 parts of 36% aqueous hydrochloric acid is added gradually at room temperature followed by the addition of three parts of urea. The reaction mass is refluxed for 16 hours, cooled, made alkaline to Brilliant Yellow paper with sodium carbonate, and steam distilled. The resinous residue is washed with cold water and dissolved in 70 parts of ethyl ether. The ether solution is clarified by passage through activated carbon and treated with anhydrous hydrogen chloride. The pale green solid which precipitates in an amount of 24 parts has the formula



Oxidation of this product with lead dioxide in methanol solution yields a gray dye which is readily adsorbed by paper. The dye exhibits absorption bands with maxima at 620 m μ and 493 m μ having an intensity ratio of 2.2.

EXAMPLE 13

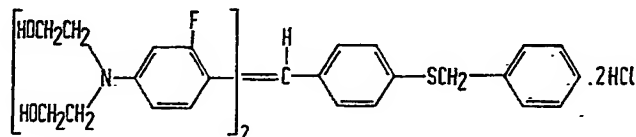
Bis(4-didodecylamino-o-tolyl) (p-benzylthiophenyl)methane

By the procedure of Example 1, 8.9 parts of N,N-didodecyl-m-toluidine and 2.3 parts of p-benzylthiobenzaldehyde are reacted in 60 parts of methanol containing one part of 36% aqueous hydrochloric acid and 0.6 part of urea to form the subject compound as a viscous oil. The product is oxidized in an acid methanol solution with lead dioxide to a dye which imparts a gray color to paper treated with the solution.

EXAMPLE 14

Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl] (p-benzylthiophenyl)methane dihydrochloride.

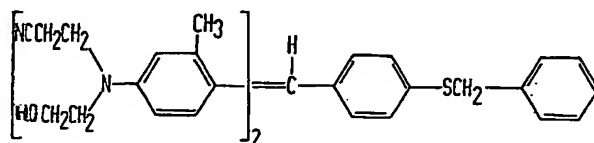
By the procedure of Example I, 14 parts of m-fluoro-N,N-bis(2-hydroxyethyl)-aniline are reacted with 7.5 parts of p-benzylthiobenzaldehyde to provide 8.8 parts of product having the formula



On oxidation in methanol solution, the subject compound gives a bluish gray dye which readily colors paper.

EXAMPLE 15

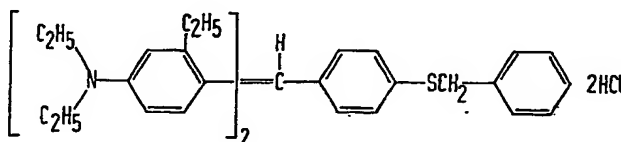
Bis[4-([2-cyanomethyl] [2-hydroxyethyl] amino)-o-tolyl] (p-benzylthiophenyl)methane.
As described in Example I, 4.1 parts of N-(2-cyanoethyl)-N-(2-hydroxyethyl)-m-toluidine are reacted with 2.3 parts of p-benzylthiobenzaldehyde to yield 4.5 parts of the subject compound as a white solid having the formula



Oxidation of this leuco dye gives a purple gray coloring material which imparts this color to paper immersed in a solution of the dye.

EXAMPLE 16

Bis(4-diethylamino-2-ethylphenyl) (p-benzylthiophenyl)methane dihydrochloride.
Under the conditions set forth in Example I, 7.1 parts of N,N-diethyl-m-ethyl-aniline and 4.6 parts of p-benzylthiobenzaldehyde are reacted to form a leuco dye in the form of its dihydrochloride having the structure

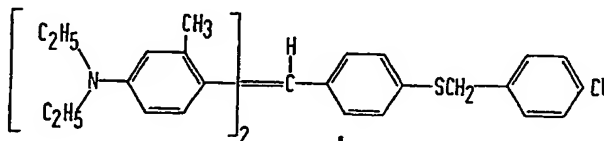


The product is a white powder which is readily oxidized to the corresponding dye having a black color.

A solution of the dye is gray, and paper sprayed with it is colored gray. The dye exhibits well defined absorption bands at 648 mμ and 500 mμ with an intensity ratio of 1.9.

EXAMPLE 17

Bis(4-diethylamino-o-tolyl) [p(p-chlorobenzylthio)phenyl]methane
As in the preceding examples, 16.3 parts of N,N-diethyl-m-toluidine and 13.2 parts of p-(p-chlorobenzylthio)benzaldehyde are reacted and form 4.5 parts of a white powder having a melting range of 75° to 77° C. and the following formula



Confirmatory analytical results are:

| Calculated for $C_{36}H_{48}N_2ClS$: | Found: |
|---------------------------------------|--------|
| %C 75.9 | 76.3 |
| %H 7.5 | 7.7 |
| %N 4.9 | 5.0 |
| %Cl 6.1 | 6.4 |
| %S 5.6 | 5.7 |

On oxidation in methanol solution, this leuco dye gives a gray colored solution.

EXAMPLE 18

Bis(4-diethylamino-o-tolyl) [p-(p-methylbenzylthio)phenyl]methane dihydrochloride
By the procedure of Example I, 16.3 parts of N,N-diethyl-m-toluidine and 12.1 parts of p-(p-methylbenzylthio)benzaldehyde are reacted to form the subject hydrochloride salt of leuco dye as a white solid in an amount of 22 parts. The oxidized product of this compound is a black dye which imparts a gray color to paper.

EXAMPLE 19

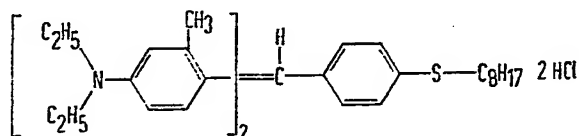
Bis(4-diethylamino-o-tolyl) (p-methylthiophenyl)methane dihydrochloride

By the procedure of Example I, 16.3 parts of N,N-diethyl-m-toluidine and 7.6 parts of p-methylthiobenzaldehyde are reacted to give 10.4 parts of leuco dye. The oxidized product of the compound is a black solid which imparts a gray color to paper.

EXAMPLE 20

Bis(4-diethylamino-o-tolyl) (p-octylthiophenyl)methane dihydrochloride

The above compound is prepared by reacting 19.6 parts of N,N-diethyl-m-toluidine and 15 parts of p-octylthiobenzaldehyde in methanol in the presence of hydrochloric acid and urea as described in Example I. After the reaction mixture is made alkaline, it is steam distilled. The gummy residue is taken up in isopropyl alcohol and purified by contact with activated charcoal and filtering. The clear filtrate is then treated with anhydrous hydrogen chloride. The precipitate that forms, dried at 50° C., is a white powder having the formula



The calculated chlorine content is 11.2%, found 10.5%. This product in water solution is readily oxidized with lead dioxide to a gray-black dye showing high tinctorial strength on paper.

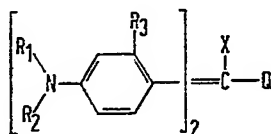
The preceding representative Examples may be varied within the scope of the present total specification disclosure, as understood and practiced by one skilled in the art, to achieve essentially the same results.

Additional representative specie compounds which are part of the present generic invention include the following:

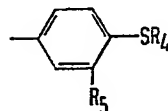
bis[4-bis(2-propoxyethyl)amino-2-fluorophenyl] (p-benzylthiophenyl)methane,
bis[4-bis(4-butoxybutyl)amino-o-tolyl] (p-butylthiophenyl)methane,
bis[4-(N-methyl-N-naphthylamino)-o-tolyl] p-(1-naphthylthio)phenylmethane,
bis[4-(N-methoxymethyl)-N-methylamino-2-ethylphenyl]-(p-benzylthiophenyl)-
cyanomethane, and
bis[4-bis(3-hydroxypropyl)amino-o-tolyl] (p-hexylthiophenyl)methanol.

WHAT WE CLAIM IS:—

1. A leuco dye of the formula:—

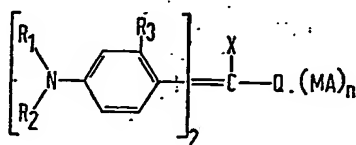


where R₁ and R₂ are alkyl groups containing from 1 to 12 carbon atoms, 2-cyanoethyl, 2-hydroxyethyl, 3-hydroxypropyl, alkoxy alkyl groups containing from 2 to 8 carbon atoms; aralkyl or aryl groups; R₃ is methyl, ethyl or fluorine; X is hydrogen, hydroxyl or cyano; and Q is 2-thienyl, 2-furyl, 3,4-methylenedioxyphenyl, 2-methoxy-4-(C₁ to C₄)-alkoxyphenyl, 3,4-di(C₁ to C₄)-alkoxyphenyl, or



where R₄ is an alkyl, aralkyl, aryl or substituted aralkyl group containing from 1 to 8 carbon atoms, the substituents of said substituted aralkyl being fluoro, chloro, alkyl or alkoxy substituents and R₅ is hydrogen or an alkyl group containing from 1 to 4 carbon atoms, and oxidised, colored forms thereof.

2. A leuco dye salt of the formula: —



where R_1 , R_2 , R_3 , X and Q are as defined in claim 1, M is hydrogen and A an anion, or M is a metal and A is an anion or anions which satisfy the valence of M and which together with M form a Lewis acid, and n is 1 or 2.

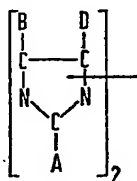
3. A leuco dye salt according to claim 2 in which M is zinc.

4. A leuco dye, salt thereof or oxidised, colored form thereof, according to any of claims 1 to 3 in which R_3 is methyl.

5. A leuco dye or colored, oxidised form thereof according to claim 1 substantially herein described in any of the Examples.

6. A leuco dye salt according to claim 2 substantially as herein described in any of the Examples.

7. A light-sensitive composition which comprises intimate admixture of a leuco dye or salt thereof according to any of claims 1 to 6 wherein X is hydrogen and a 2,4,5-triarylimidazolyl dimer of the formula: —



where A, B and D are alike or different and are non-substituted or substituted radicals of homo- and heterocyclic aromatic systems, said dimer being dissociated into free radicals when irradiated with ultraviolet light.

8. A composition according to claim 7 which also comprises an inert solvent and/or an inert transparent binder.

9. A light sensitive composition according to claim 7 or 8 substantially as herein described in any of the Examples.

10. A light sensitive material which comprises a supporting base material carrying a light sensitive composition according to any of claims 7 to 9.

11. Paper treated with a light sensitive composition according to any of claims 7 to 9.

12. A process for forming a coloured material which comprises irradiating a light sensitive composition according to any of claims 7 to 9 with radiation having a wavelength of from 2000 Å to 4200 Å.

13. A process according to claim 12 which also comprises subjecting the coloured material to a fixing treatment.

14. A process according to claim 12 or 13 substantially as herein described in any of the Examples.

15. A light sensitive composition which comprises a leuco dye or salt thereof according to any of claims 1 to 6 and a halogen-containing hydrocarbon which generates halogen-free radicals upon exposure to radiation of a suitable wave-length.

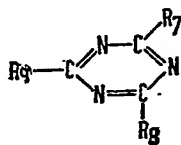
16. A composition according to claim 15 in which the halogen-containing hydrocarbon is carbon tetrabromide.

17. A composition according to claim 15 or 16 which also comprises an inert solvent and/or an inert binder.

18. A light sensitive composition according to any of claims 15 to 17 substantially as herein described in any of the Examples.

19. A light sensitive material which comprises a supporting base carrying a light-sensitive composition according to any of claims 15 to 18.

20. A light - sensitive composition which comprises a leuco dye or salt thereof according to any of claims 1 to 6 in which X is a cyano group and a cyanuric acid compound of the formula: —



where R₇, R₈ and R₉ are hydroxy, chlorine, and OX, X in said OX is an alkyl, alkenyl, cycloalkyl, aryl, aralkyl, or alkaryl group containing up to 18 carbon atoms.

21. A composition according to Claim 20 wherein said cyanuric acid compound is triallylcyanurate. 5

22. A composition according to claim 20 or 21 which also comprises an inert solvent and/or an inert, transparent binder.

23. A composition according to any of claims 20 to 22 substantially as herein described in any of the Examples.

24. A light sensitive material which comprises a supporting base carrying a light sensitive composition according to any of claims 20 to 23. 10

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